

A27

PCT

World Intellectual Property Organization  
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY  
(PCT)

(51) International Patent Classification<sup>5</sup>:

C09K 7/06, B01F 17/18

A1

(11) International Publication Number: WO 92/19693

(43) International

Publication Date: November 12, 1992 (12/11/92)

(21) International Application Number: PCT/EP92/00920

(22) International Filing Date: April 28, 1992 (04/28/92)

(30) Priority Data:

P 41 14 906.8 May 7, 1991 (05/07/91) DE

(71) Applicant (for all designated states except the US):

HENKEL KOMMANDITGESELLSCHAFT  
AUF AKTIEN [HENKEL LIMITED  
PARTNERSHIP WITH STOCK] (DE/DE);  
Henkelstrasse 67, D-4000 Dusseldorf 13 (DE).

(72) Inventor; and

(75) Inventor/Applicant (only for US): PONSATI, Oriol  
(ES/ES); 2 de Mayo, 260-4-1, E-08025 Barcelona  
(ES). TRIUS, Antonio (ES/ES); Po de la  
Orquidea 75-77 Valldoreix, E-08190 Sant Cugat  
(ES). HEROLD, Claus-Peter (DE/DE);  
Ostpreussenstrasse 26, D-4020 Mettmann (DE).  
MUELLER, Heinz (DE/DE); Rehwechsel 2, D-  
4019 Monheim (DE). NITSCH, Christian  
(DE/DE); Otto Hahn Strasse 185, D-4000  
Dusseldorf 13 (DE). VON TAPAVICZA,  
Stephan (DE/DE); Thomas Mann Strasse 12, D-  
4006 Erkrath (DE).

(74) Joint Representative: Henkel KOMMANDITGE-  
SELLSCHAFT AUF AKTIEN; TFP / Patent  
Department, P.O. Box 10 11 00, D-4000  
Dusseldorf 1 (DE)

(81) Designated States: AT (European patent), BE  
(European patent), BR, CH (European patent),  
DE (European patent), DK (European patent),  
ES, (European patent) FR (European patent),  
GB (European patent), GR (European patent),  
IT (European patent), JP, LU (European  
patent), MC (European patent), NL (European  
patent), SE (European patent), US.

Published

*With international search report.*

*Before expiration of the time period allowed for the  
changing of claims. Publication will be repeated if  
changes occur.*

(54) Title: USE OF SELECTED OLEOPHILIC COMPOUNDS WITH QUATERNARY NITROGEN  
TO IMPROVE THE OIL WETTABILITY OF FINELY DIVIDED CLAYS AND THEIR  
USE AS VISCOSITY PROMOTERS

(57) Abstract

[ English-language Abstract, see original German document ]

Best Available Copy

**"Use of Selected Oleophilic Compounds with Quaternary Nitrogen to Improve the Oil Wettability of Finely Divided Clays and Their Use as Viscosity Promoters"**

The invention pertains to new possibilities for influencing and controlling the rheology of non-aqueous liquid phases, and, in particular, makes possible a controlled thixotropic viscosity buildup in liquids of this type.

The predetermined regulation of the rheological behavior of non-aqueous liquid phases has considerable importance in many technical fields. One important example of this are the drilling fluids that are widely used today, which are based on so-called invert emulsions that contain a dispersed aqueous phase within a closed oil phase. One important area of application for such drilling fluid systems is in off-shore boring for the development of crude petroleum and/or natural gas deposits. Today, however, such W/O emulsions are also widely used for land-supported boring, for example, in geothermal drilling, exploratory boring for water, in carrying out geotechnical boring and for boring in the mining industry.

In one important form of implementation, the invention pertains to improved drilling fluids of this type of W/O invert system, so that in the following, particular reference will be made to that area of application, even though the invention is not in any way limited to that. Drilling fluid systems of the type under discussion here contain, dissolved and/or dispersed in flowable oil phases of selected rheology, a multiplicity of additives whose presence ensures the usability of the particular system under field conditions. Reference is made to the relevant literature, by way of example, to the publication of Adam T. Bourgoyne, Jr. et al., *APPLIED DRILLING ENGINEERING, SPE TEXTBOOK SERIES, VOL. 2, SOCIETY OF PETROLEUM ENGINEERS*, Richardson, TX, 1986, especially the sub-chapter 2.5, Oil Muds, Op. Cit., pages 75 through 81.

In contemporary practice, hydrophobized layer silicates from the bentonites group are used as rheology-regulating additives for non-aqueous drilling fluids. Such products are commercially available under the collective designation "Bentone<sup>®</sup>", for example. The hydrophobizing of the clays needed in order to incorporate them into the slightly polar to non-polar carrier liquid is usually carried out by means of quaternary ammonium salts whose organic cations combine with the negatively charged layer silicate lamina by means of electrostatic interactions. While such products are indeed satisfactory from a technological standpoint, they must be considered problematic from ecological perspectives. The quaternary ammonium salts being used at present for the hydrophobizing are resistant to degradation, and generally show biocidal effects, so that harm to the environment cannot be excluded.

The invention begins with the task of making available substitutes that are ecologically less questionable but at least equivalent in technical practice for influencing and controlling the rheology of such non-aqueous liquid phases. The technical solution to this task begins with the knowledge that a selected, long-known subclass of quaternary ammonium compounds is qualified to meet the technical requirements for the oleophilic equipping of such clays, and thus the technical requirements for their use in oil phases, but that this selected subclass of quaternary ammonium compounds is also characterized by great environmental compatibility. The subclass from the group of quaternary ammonium compounds that is used in accordance with the invention and is described in detail in the following is derived from alkylolamine compounds whose hydroxyl groups are at least partially esterified with carboxylic acids, and in this way form a molecule with pronounced oleophilic properties. Compounds of the type affected by the invention are designated in the following as "esterquats". They are characterized by adequate stability in their application and when used with the clays thus equipped, but they are at the same time - probably as a result of their ester groupings - so unstable in living biological systems that in the field of oleophilically equipped clays affected by the invention, previously unknown ecological compatibilities can be stopped. That also holds true in particular for the marine area, which is known to be especially sensitive, so that as a result of the science of the invention, the goal of averting ecologically harmful

consequences when working with W/O invert emulsions, when used as in drilling fluids in sea-supported boring, can be further optimized.

#### The science of the invention

Accordingly, the object of the invention in a first form of execution is the use of quaternary oleophilic esters of alkylolamines and carboxylic acids with at least 8 C atoms in the carboxylic acid molecule (esterquats) to hydrophobize and extend the oil wettability of natural and/or synthetic clays for their use in oil-based liquid phases, especially as viscosity promoters in flowable drilling emulsions of the W/O invert emulsion type.

In an additional form of execution, the invention pertains to oil-dispersible thickening agents and possibly other components, especially borehole treatment agents which may be used in the context of land- and/or sea-supported rock boring, with the feature that they contain at least a proportion of finely divided synthetic and/or natural clays that have been treated with the previously defined esterquats as oil-dispersible thickening agents

Finally, the invention pertains to the finely distributed clays of natural and/or synthetic origin that are equipped with the represented esterquats, particularly the corresponding swellable clays of the montmorillonite type. The classical example of corresponding clays of natural origin are the bentonites, while greater or less swellable synthetic clay compounds of the type under discussion here can be assigned in particular to the class of the smectites, e.g., the hectorites. The loading of these clay dosing materials with the esterquats selected in accordance with the invention for oil-dispersible and rheologically effective thickening agents can be carried out in way that is known per se, as, according to previous practice, the corresponding clays are equipped with the quaternary ammonium compounds that have been common until now.

#### Specifics regarding the esterquats selected in accordance with the invention

The class of condensation products of alkylolamines and higher fatty acids that have been quaternized with the common quaternization agents such as dimethyl sulfate,

diethyl sulfate, methyl halogenides such as methyl chloride, etc., as well as selected applications for compounds of this type, are known. Reference can be made, for example, to US-PS 3 915 867, in which it is described that this class of material is basically known as textile softeners and possibly as surface-active agents. The science of this U.S. patent selects for the purpose of textile softening specifically delimited compounds of the type under discussion here, which meet the requirement profile of the application described therein especially well. The selected class of materials involves N-alkyl-N,N-di(B-C<sub>14</sub>-C<sub>18</sub>-acyloxy-ethyl)-N-B-hydroxy-ethyl quaternary ammonium compounds.

The science of the invention includes esterquats of this type, but is not limited to it. That is easily understood from the different requirement profile that is demanded for, first, a textile softener, and second, for equipping oleophilic clay for technical uses in the sense of the science of the invention. Any kind of references to the suitability of the class of esterquats for the task according to the invention, the ecologically improved oleophilic equipping of viscosity promoters on the basis of swellable clays particularly for the closed oil phases cannot be found in the state of the art.

According to the invention, those esterquats are preferred whose ester-forming acid residues are derived from monocarboxylic acids, preferably with at least 12 C atoms. Particularly well-suited in this instance are markedly oleophilic long-chain carboxylic acids or carboxylic acid residues with, for example, up to 32 C atoms, in particular, with up to 24 C atoms. The carboxylic acid residues can be at least partially singly or multiply olefinically unsaturated, whereby similar carboxylic acid residues or a mixture of different ones can be present in the esterquats.

In a preferred form of execution of the invention, residues of straight-chain carboxylic acid are present in the esterquats at least partially, in particular, at least preponderantly. The ecological compatibility of such acid residues, expressed as aerobic or anaerobic degradability, is known to be particularly high. The preferred acids or acid residues in the esterquats in the sense of the science of the invention are those of natural origin, whereby any kind of saturated and/or unsaturated acid

mixtures in the range from  $C_{12}$  to  $C_{22}$  are easily accessible and especially effective representatives. Known starting materials for the preparation of these monocarboxylic acids are vegetable and/or animal oils. Mention can be made of coconut oil, palm nut oil and/or babassu oil, in particular as base materials for the preparation of monocarboxylic acids primarily in the range up to  $C_{18}$  and of essentially saturated components. Vegetable ester oils for singly and possibly multiply olefinically unsaturated carboxylic acids in the range from  $C_{16}$  to  $C_{24}$  are, for example, palm oil, peanut oil, castor oil, sunflower oil, and especially rape oil. Carboxylic acids of this type of animal origin are, in particular, suitable mixtures of tallow and/or fish oils such as herring oil.

In the esterquats that are to be used in accordance with the invention, these carboxylic acid residues in ester form are combined with and by means of the hydroxyl group of alkylolamines. Preferred in this regard are alkylolamines that exhibit at least partially more than one hydroxyl group in the base molecule; particularly well-suited as the building block are the corresponding alkylolamines that can make available up to 5 and preferably 2 and/or 3 hydroxyl groups for potential esterification with the oleophilic monocarboxylic acids. In conjunction with that, it can be desirable that in the esterified alkylolamine more than one carboxylic acid residue is at least partially combined, whereby, however, it is not necessary that all hydroxyl groups of the alkylolamine being used are reacted to completion with the carboxylic acid residues. Thus, corresponding esters which - depending on the number of available free hydroxyl groups in the alkylolamine being used - can be especially well-suited exhibit 2 to 4 and, especially 2 and/or 3 carboxylic acid residues. If, for example, alkylolamines with 3 hydroxyl groups are used as the esterquat-forming component, their esterification products which contain in predominant quantity 2 hydroxyl groups esterified with the monocarboxylic acids can be especially well-suited, but along with that, they exhibit singly and triply esterified residues of the alkylolamine in statistical distribution.

The following data are valid for defining the base component of the alkylolamines: Preferred for use within the context of the invention are esterquats that are derived from alkylolamines with up to 15 C atoms in the molecule, and preferably with up

to 8 C atoms. In conjunction with that, the N function can be present in the alkylolamine either simply or multiply. It is beneficial for the alkylolamines to contain no more than three N groups, whereby those compounds of this type that exhibit only one N group in the molecule are specially preferred. Derived finally from this is the class of the most important esterquats in the sense of the invention, those containing a tertiary N group in the molecule.

Both for reasons of technical accessibility as well as reasons of ecological compatibility and, especially, biological degradability, those alkylolamines whose alkylol residues develop straight-chain and with terminal hydroxyl groups are preferred for the production of the esterquats. The most easily accessible representatives of this class of compound from the technical sense contain corresponding ethanol residues, so that esterquats based on ethanolamine compounds take on special importance. In turn, the preferred representative for this building block is that triethanolamine whose hydroxyl groups are at least partially esterified with the carboxylic acids. Corresponding mixed esters with a predominant proportion of two carboxylic acid residues that contain in subordinate quantity singly esterified and triply esterified triethanolamine in the molecule, can be especially well-suited base materials for the quaternization, and thus for the equipping of clays with the esterquats.

The quaternizing of the alkylolamine ester takes place in a way that is known per se, for example, through reaction with alkyl halogenides, dialkyl sulfates, etc. Dimethyl sulfate or methyl chloride are characteristically known representatives of this reaction, in which regard additional reference can be made to generally known chemical science.

The clays to be oleophilically equipped in accordance with the invention

Suitable clay materials, in particular, colloiddally soluble and/or dispersible clays of natural and synthetic origin are the subject matter of extensive publications, so that reference can be made to the latter.

With regard to natural clays and their interaction with oil phases, especially their

loading with quaternary ammonium compounds, reference can be made to the publication "Clay Colloid Chemistry", H. van Olphen, John Wiley and Sons, 2nd Edition (1977), and specifically to Chapter 11, "Interaction of Clays and Organic Compounds", op. cit. Pp. 162-200. As has already been indicated, the most important clay material used for large-scale technical purposes is the swellable bentonite of natural origin, the oleophilic equipping of which is a preferred form of execution in the sense of the science of the invention as well.

Synthetic clay materials used are, in particular, water-swellable smectite clays, for example, highly swellable hectorites, saponites and/or saponite-hectorite hybrids. However, clays of the attapulgite or sepiolite type can be suitable as well.

The synthesis of layer silicates, especially of hectorites, has been described often in the literature (H. Strese and U. Hoffmann, Z. Anorg. Allg. Chem. [Journal of Inorganic General Chemistry] 247 (1941), 65-95; W.I. Grandquist and S.S. Pollack in "Clays and Clay Minerals", Nat'l Acad. Sci., Nat'l Res. Council Publ. 8 (1960), 150-169; DE-AS 1 667 502). A more recent place in the literature deals extensively with the knowledge that is available today with regard to the structure, genesis and production of hectorite, cf. Karl-Heinz Bergk et al., Chem. Techn. 41 Jg., Vol. 6, 245-251. In the last-cited place in the literature, particular reference is made to the possibility of oleophilically equipping these synthetic minerals (cf. Op. Cit. P. 250).

With regard to the mechanism of the application of the quaternary ammonium compounds to the particular clay mineral to be equipped, reference can also be made to the extensive published state of the art, such as is represented in the cited place in the literature, H. van Olphen, "Clay Colloid Chemistry, 171-173, and especially the publications for numbers 15-36 in the reference list for this sub-chapter.

The use of esterquat-equipped clays in oil phases, especially W/O invert emulsions. Clays oleophilically equipped with esterquats in the sense of the invention can be used in the broadest possible range of applications. What is advantageous is the fact that extensive studies have not only shown high ecological compatibility in the sense of satisfactory degradability under aerobic and anaerobic conditions, it has been



established in addition that, for example, esterquats based on TEA derivatives with fatty acids of natural origin, also trigger no skin irritation on living bodies. From the numerous applications that derive from that for oleophilically equipped clays of that type and their use as thickening agents in oil phases, represented in the following by way of example is the use in the field of borehole treatment agents, specifically, the drilling fluid agent for rock boring.

Oil-based fluid systems in which the oil forms the flowable phase, or at least the predominant proportion of the flowable phase, are in practical use in a broad range of applications. Of special importance here are the so-called invert drilling fluid muds, which, on the basis of W/O emulsions, contain a disperse aqueous phase in the closed oil phase. The content of a disperse aqueous phase usually lies in the range of about 5 to 50 weight percent. The aqueous phase is generally distributed heterogeneously finely dispersed in the closed oil phase. A plurality of additives are provided, especially emulsifying agents, weighting agents, fluid-loss additives, alkali reserves, viscosity regulators, etc. For further details, reference can be made, by way of example, to the publication of P.A. Boyd et al., "New Base Oil Used in Low-Toxicity Oil Muds", Journal of Petroleum Technology, 1985, 137-142, and to R.B. Bennett, "New Drilling Fluid Technology - Mineral Oil Mud", Journal of Petroleum Technology, 1984, 975-981, as well as the literature cited therein.

The oil phases of drilling fluids of the type under discussion here and comparably structured borehole treatment agents are formed almost exclusively by means of mineral oil fractions. Associated with that is not inconsiderable harm to the environment if, for example, the drilling muds get into the environment either directly or via the drilled rock. Mineral oils are very difficult to degrade and practically impossible to degrade anaerobically, and thus must be considered as long-term pollution.

In a large number of older patent rights, the applicant describes suggestions for replacing the mineral oil fractions with ecologically compatible, easily degradable oil phases. Four different types of substitute oils are presented in that regard, which can also be used mixed with each other. This involves selected oleophilic monocarboxylic

acid esters and corresponding polycarboxylic acid esters, flowable alcohols that are at least largely insoluble in water under working conditions, corresponding ethers and selected carbonic acid esters. By way of summary, reference is made to the publications and older applications DE-A-38 42 659, DE-A-38 42 703, DE-A-39 07 391, DE-A-39 07 392, DE-A-39 03 785, DE-A-39 03 784, DE-A-39 11 238, DE-A-39 11 299, DE-A-40 19 266, and DE-A-40 18 228. All of the applications cited here pertain to the field of oil-based fluid systems, especially of the W/O invert type.

In a preferred form of execution of the invention, the viscosity regulation of such ecologically compatible oil phases, which are degradable through natural degradation processes, takes place by means of the oleophilically adjusted clays described by the invention, including the use of esterquats.

In an additional form of execution, the invention provides the following modification, which also serves the goal of making available ecologically improved working materials for the field under discussion.

The object of the applicant's older application DE-A-40 12 105 is the use of hydrogenated castor oil in place of organophilic quaternized clays for viscosity control and, especially for spontaneous viscosity buildup in oil-based drilling fluids for the development of geological deposits. In accordance with the invention, a combination of the viscosity promoters based on clays oleophilically equipped with esterquats and the hydrogenated castor oil can now be used, whereby practically any desired mixing ratios between 5 and 95 weight percent for the two components, for example, can be set. In a preferred form of execution, at least approximately equal-quantity proportions of clays oleophilically equipped with esterquats are used with the hydrogenated castor oil.

In an even more preferred form of execution, the invention's goal of increased ecological compatibility in the borehole treatment agents of the W/O type is additionally taken into consideration that ecologically compatible emulsifying agents are used at the same time. Here as well, reference can be made to a series of the applicant's older patent rights, the co-application of which within the context of the

science of the invention brings with it the advantages that are being sought.

Suitable emulsifying agents in this sense are, especially surface-active alkyl glycoside compounds such as those described in DE-A-40 24 658, surface-active alpha-sulfonic fatty acid di-salts per DE-A-40 24 659, surface-active ester sulfonate salts per DE-A-40 24 892, and surface-active carboxylic acid complex esters per DE-A-41 02 908. The disclosure contents of these older patent rights is also hereby expressly made an object of the present invention disclosure as well.

It holds uniformly true for all oil phases or oil mixed phases in accordance with the invention, that flash points of at least about 100°C and preferably flash points above about 135°C are required for safety reasons during operations. Values that are clearly higher, in particular, those above 150°C, can be especially beneficial. It holds true in addition, that the ester-based oleophilic clays in flowable and pumpable invert systems are brought into use in closed oil phases that exhibit congealing points (pour point and setting point of the oil phase) below 0°C, preferably below -5°C, and possess in conjunction with that a Brookfield (RVT) viscosity of not more than 55 mPas, preferably not more than 45 mPas, in the temperature range from 0 to 5°C. In addition, it holds uniformly true for the various potential hydrolysis-endangered oil phases that can be used within the context of the invention, that the requirement of ecological compatibility is not just met for the compound that is being used, for example, the specifically selected ester oil or mixture of ester oils, but that in addition, no toxicological and, in particular, no inhalation toxicological hazards are triggered, even in the event of partial saponification. It is expressly described within the context of the cited older applications, that the various representatives of the ester oils are addressed in particular there, whereby mono-functional alcohols from the ester forming are also given special importance there. In comparison with poly-functional alcohols, mono-functional alcohols are highly volatile in their lower links, so that secondary hazards can occur here as a result of partial hydrolysis. Accordingly, in the classes of the various ester oils, co-applied mono-functional alcohols or the corresponding residues of these alcohols are selected in such a way that they possess at least 6 C atoms in the molecule, and preferably at least 8 C atoms. Hydrolysis-stable ether can be especially important for practical use as a

closed oil phase of the borehole treatment agents.

For invert drilling fluids of the type dealt with by the invention, it holds true, independently of the specific nature of the closed oil phase, that they exhibit in preferred forms of execution a plastic viscosity (PV) in the range from approximately 10 to 60 mPas and a yield point (YP) in the range from 5 to 40 lb/100 ft<sup>2</sup>, determined in each case at 50°C.

Along with ethers from alcohols of natural and/or synthetic origin, what have proven to be oil phases that are particularly ecologically compatible and easily flowable at lower temperatures are ester oils of monocarboxylic acids, which, in a preferred form of execution of the invention, derive from at least one of the following subclasses:

- a) Esters of C<sub>1-5</sub> monocarboxylic acids and single- and/or multiple-function alcohols, whereby residues of monohydric alcohols exhibit at least 6, preferably 8 C atoms and the polyhydric alcohols preferably possess 2 to 6 C atoms in the molecule,
- b) Esters of monocarboxylic acids of synthetic and/or natural origin with 6 to 16 C atoms, in particular esters of corresponding aliphatic saturated monocarboxylic acids and single- or multiple-function alcohols of the type mentioned under a),
- c) Esters of olefinic singly and/or multiply unsaturated monocarboxylic acids with at least 16, in particular 16 to 24 C atoms and, in particular, mono-functional straight-chain and/or branched alcohols.

Base material for the preparation of numerous monocarboxylic acids that fall into these subclasses, especially those with a higher carbon value, are vegetable and/or animal fats and/or oils. Tallow, coconut oil, palm nut oil and/or babassu oil can also be mentioned again here, in particular as materials to be used for the preparation of monocarboxylic acids primarily in the range up to C<sub>18</sub> and of essentially saturated components. Vegetable ester oils, especially for singly and possibly multiply olefinically unsaturated carboxylic acids in the range from C<sub>16</sub>-C<sub>24</sub> are, for example, palm oil, peanut oil, castor oil, sunflower oil, and especially rape oil. However, synthetically prepared components are also important structural elements for

ecologically compatible oil phases both on the carboxylic acid side as well as on the side of the alcohols.

#### Additives in oil-based fluid

Invert drilling fluid muds generally contain, along with the closed oil phase, the finely dispersed aqueous phase in quantities of about 5 to 50 weight percent. Along with the water content, all of the additives provided for comparable fluid types come into consideration. These additives can be water-soluble, oil-soluble and/or water- or oil-dispersible.

Common additives, along with the clays defined by the invention, are, by way of example, emulsifying agents, fluid-loss agents, additional soluble and/insoluble materials for building structural viscosity, alkali reserves, agents for inhibiting the unwanted dispersion of water between drilled formations - e.g., water-swellable clays and/or salt deposits - and the drilling fluid liquid, wetting agent for improved absorption of the oil phase on solid surfaces, e.g., for improving the lubricating effect, but also for improving the oleophilic closure of uncovered rock formations or rock surfaces, biocides, for example, to inhibit bacterial attack on the emulsions, etc. Specific reference is to be made here to the relevant state of the art as it is described extensively, for example, in the technical literature cited earlier, cf. in particular Gray and Darley, op. cit., Chapter 11, "Drilling Fluid Components". Accordingly, only excerpts will be cited:

Finely dispersed additives to increase the fluid density: Barium sulfate (barite) is in widespread use, but calcium carbonate (calcite) or the carbonate mix of calcium and magnesium (dolomite) are also used.

Unwanted dispersion of water by means of, for example, clays with inhibiting additives: Coming into consideration here are the additives known from the state of the art of oil-based drilling fluids. In particular, this involves halogenides and/or carbonates of the alkali and/or alkaline earth metals, whereby corresponding potassium salts, possibly in combination with lime, can become especially important. More recent suggestions provide for the use of lower water-soluble alcohols such as

glycerine and/or propandial, cf., for example, GB 2 223 255-A. By way of example, reference can also be made to the publications in "Petroleum Engineer International", September 1987, 32-40, and "World Oil", November 1983, 93-97.

Alkali reserves: Coming into consideration here are inorganic and/or organic bases matched to the overall behavior of the fluid, in particular, corresponding basic salts or hydroxides of alkali and/or alkaline earth metals, as well as organic bases. Lime is an especially important representative of this class. The type and amount of these basic components are matched to each other in a known way.

The amount of the particular emulsions and additives used basically varies within the usual range, and can thus be taken from the cited relevant literature.

### Examples

Using a synthetically prepared finely divided clay sold under the trade name "Dehydril HT<sup>®</sup>" that is hectorite-based and is highly swellable in aqueous systems, a 3 weight percent colloidal solution with a gel structure is produced. The oleophilic and quaternary nitrogen-containing esterquat-based component that is defined in the following is mixed at room temperature in stoichiometric excess for a period of about 0.5 hours, with intensive stirring of the thixotropic aqueous gel. The gel structure breaks down in proportion to the addition of the esterquat compound to the aqueous hectorite gel. The oleophilic reaction product that is formed flocculates in the aqueous phase. Subsequently, a secondary reaction is carried out while stirring for an additional 0.5 hours in the temperature range from 40 to 45°C.

The solid phase that now occurs is separated from the aqueous phase by means of filtration, and is then washed with water. The filter residue is dried at 70°C and then comminuted into a finely powdered material.

Using this hydrophobized synthetic clay as a viscosity promoter, an oil-based drilling fluid system of the W/O type is put together, whereby the closed oil phase is formed by means of the oleophilic carboxylic acid ester mixture defined in the following:

Ester mixture comprised in essence of saturated fatty acids based on palm nut and 2-ethyl hexanol, which originates to by far the greatest extent from C<sub>12/14</sub> fatty acids and which meets the following specifications:

C<sub>8</sub>: 3.5 to 4.5 weight percent

C<sub>10</sub>: 3.5 to 4.5 weight percent

C<sub>12</sub>: 65 to 70 weight percent

C<sub>14</sub>: 20 to 24 weight percent

C<sub>16</sub>: approx. 2 weight percent

C<sub>18</sub>: 0.3 to 1 weight percent

The ester mixture is present as a light yellow liquid with a flash point above 165°C and a viscosity (Brookfield 20°C) of 7 to 9 cp.

The W/O invert drilling fluid system is combined in accordance with the following recipe in a manner that is known per se:

To 130 ml carboxylic acid ester oil

6 g W/O emulsifying agent (INVERMUL NT from the firm of Baroid Drilling Fluids Inc.)

26 ml water

6 g organophilic hectorite in accordance with the invention

12 g organophilic lignite (DURATONE from the firm of Baroid Drilling Fluids Inc.)

2 g lime

6 g W/O emulsifying agent (EZ-MUL NT from the firm of Baroid Drilling Fluids Inc.)

346 g barite

9.2 g  $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$

The viscosity characteristic value for unaged and aged material is determined as follows:

Measurement of the viscosity at 50°C in a Fann 35 viscosimeter from the firm of Baroid Drilling Fluids Inc. In a manner that is known per se, the plastic viscosity (PV) in mPas, the yield point (YP) in lb/100 ft<sup>2</sup>, and the gel strength (lb/100 ft<sup>2</sup>) after 10 seconds and 10 minutes are found. In addition, the emulsion stability (ES) is found in volts (V).

The aging of the given drilling fluid is carried out through treatment in an autoclave - a so-called roller oven - for a period of 24 hours at 125°C.

The characteristic values that are found for the unaged and aged material - as indicated above - are listed in the following tabular summary:



| Test                                    | Unaged material | Aged material |
|---|-----------------|---------------|
| Plastic viscosity (PV)                  | 31              | 41            |
| Yield point (YP)                        | 9               | 16            |
| Gel strength ( lb/100 ft <sup>2</sup> ) |                 |               |
| 10 seconds                              | 4               | 3             |
| 10 minutes                              | 4               | 7             |
| Emulsion stability (ES)                 | 303 V           | 1,004 V       |

Used as the hydrophobizing esterquat component in conjunction with that was a reaction product, quaternized with a methyl group, comprised of triethanolamine (TEA) and a fatty acid mixture based on coconut - primarily saturated fatty acids in the range C<sub>12-18</sub>. This esterquat component involves a mixture of materials that is for the most part formed from the corresponding diester of the TEA, and the rest from monoesters and triesters of the TEA.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**